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Chemistry of corrosion inhibitors

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Abstract

In the last quarter century, it has become feasible to extend the life of reinforced concrete structures by inhibiting chloride-induced corrosion of steel. Chemical interactions can occur between the concrete system and the inhibitor-steel-chloride system. The chemical reactions of the corrosion process in concrete and of the most commonly used inhibitors are discussed, with special attention to test procedures and practical issues arising from use of inhibitors.

Keywords: Admixtures; Air entrainment; Aminoalcohols; Calcium nitrate; Calcium nitrite

1. Introduction

A number of commercial corrosion inhibitors are marketed for use in reinforced concrete. They are added to counteract chloride ion, which is generally considered to be the corrosive agent. The cations which diffuse along with chloride into the concrete environment (usually sodium, calcium or magnesium) do not change the corrosion process significantly. Steel rebar does not corrode without water, and even in water, will not corrode without chloride, at least not appreciably at the high pH of concrete [1]. A deeper consideration reveals that oxygen has the most detrimental effect; chloride is only the catalyst. Oxygen is the element that binds the electrons originally associated with the iron atoms and it is the abstraction of these electrons which allows some iron atoms to dissolve as ferrous ions and then to precipitate as ferric oxides. Without oxygen, steel rebar will not corrode in alkaline water even with chloride present [2].

The use of corrosion inhibiting admixtures has grown over the last 25 years because they provide a level of protection and longevity that would be too difficult (essentially too expensive) to achieve otherwise. Understanding how they function is an ongoing process that relies on field experience to identify the most important issues and on theory to untangle and describe the individual effects. Corrosion inhibitors interfere with the corrosion process without detrimental effects on concrete quality—but this is not to say that corrosion inhibitors have no effect except on corrosion. In general, the effects of an inhibitor are (1) to raise the level of chloride ion necessary to initiate corrosion and (2) to decrease the rate of corrosion even if it starts. Additives which reduce the ingress of chloride ion are not categorized as corrosion inhibitors, yet they may have a corrosion-reducing effect. Cement itself is thought to have the ability to bind some chloride ion [3].

The chemistry involved in corrosion of steel in concrete crosses several disciplinary boundaries. Electrochemistry is important, of course, but in reinforced concrete applications, chemical interactions involving the cement are just as important as reactions involving the steel for an understanding of corrosion-induced failure. Other fields of chemistry which are involved are (1) inorganic chemistry, to describe the reactions of some inhibitors and of cement, which might properly belong in a class by itself, (2) organic chemistry, to describe some inhibitors and their action, (3) physical chemistry, to address diffusion and freeze–thaw, and (4) analytical chemistry, for determination of concentrations of additives and chloride, and instrumentation especially at the research level, for examination of sites of inhibitor bonding and corrosion initiation and rates of corrosion.

2. The rebar—the corrosion process

The central reaction in the corrosion process of steel is over-simplified by Eq. (1):

$$Fe^0 = Fe^{++} + 2e^- \tag{1}$$

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The reactions affecting corrosion in concrete are numerous and far more complicated [4]. Ferrous ions are soluble enough to travel some distance, especially under corrosion conditions, in the presence of chloride ions and reduced pH. If these ferrous ions, usually a pale green in color, all reached the surface of the concrete, they would be easily oxidized by air to ferric ion, and would precipitate there as one of several reddish, brown or black oxides (which are hydrated to some extent) (Eqs. (2)–(4)).

$$O_2 + 2H_2O + 4e^- = 4OH^- \tag{2}$$

$$Fe^{++} = Fe^{+++} + e^- \tag{3}$$

$$\begin{aligned} &x\mathrm{Fe}^{++} + y\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} \\ &\quad = \mathrm{Fe}_3\mathrm{O}_4, \mathrm{Fe}_2\mathrm{O}_3, \mathrm{Fe(OH)}_3, \mathrm{Fe(OH)}_3 \cdot 3\mathrm{H}_2\mathrm{O} \end{aligned} \tag{4}$$

If, on the other hand, the precipitate formed rapidly enough and close enough to the site of corrosion, it might stifle corrosion. In uninhibited concrete, most of the ferrous ions travel some distance from the corroding anode site, but do not make it completely out of the concrete before precipitating. These oxides have a greater volume (by a factor of two to four [4]) than the iron which was consumed by corrosion and can generate expansive stresses which lead ultimately to cracking of the concrete. Expansive reactions are not well understood. How can a space be filled by a precipitate and then continue to be filled even more [5]? One possibility is that the first precipitate could contain some ferrous iron. After filling a void space, electron transfer out of this precipitate to yield more ferric ion would cause water to be attracted into the precipitate, swelling it somewhat like the hydration of calcium oxide (which is used as an expansive demolition agent). Damage to the concrete, more so than loss of steel by corrosion, is the first sign of failure of reinforced concrete.

The rebar–concrete combination is a composite material which works best when the two materials are bonded together. A slightly rusty rebar (not one with flaking rust!) has better bond to the concrete than a smooth, bright rebar [6]. A slightly rusty rebar in chloride-free concrete does not corrode further, but is rendered kinetically inactive, or "passive" (very slow to corrode though not thermodynamically inert) by the alkaline environment [2]. Semi-protective coatings made of softer materials on the rebar may lead to reduced bond, and under continuously wet conditions, may not even prevent water from migrating through the coating, permitting extensive corrosion [7–10].

A film of oxides between 17 and 50 Å thick is thought to form on bare steel, providing a barrier to corrosion. Some very small current of ferrous ions makes it into solution (*from* this film or *through* it), and the presence of chloride ion in some way increases this migration; the passive barrier becomes less effective at holding iron ions inside. Finally, at some point, the film ceases to exist and is replaced by an anodic site.The mechanism by which chloride ion accelerates corrosion of steel is complex and incompletely understood, but one or more of the following descriptions [11] may be appropriate:

(1) Penetration of oxide film by chloride ion.
(2) Adsorption of chloride ion rather than a passivating species.
(3) Field effect of chloride ion pulling ferrous ions out of the metal.
(4) Catalysis of corrosion reaction by a bridging structure.
(5) Complex formation between chloride ion and some form of iron.

3. The concrete—reactions of cement with inhibitors

3.1. Initial set of concrete

Cement is a finely ground mixture of calcium silicates and calcium aluminates which reacts with water in stages. Tricalcium aluminate ($3CaO \cdot Al_2O_3$, or, in cement terminology, C_3A) and calcium aluminoferrite, ($4CaO \cdot Al_2O_3$. Fe_2O_3 or C_4AF, of somewhat variable composition) begin to react with water within a few minutes. These compounds absorb water and do not generate much strength, but can stiffen the mix and reduce workability, so a few per cent of gypsum ($CaSO_4 \cdot 2H_2O$) or plaster ($CaSO_4 \cdot 1/2H_2O$) is added to control the fluidity until tricalcium silicate can begin to hydrate (after a few hours). Then much later, dicalcium silicate contributes to the strength. Initial set is a stiffening which allows finishing after a few hours, but it is only the beginning of the strength development of concrete, which is conventionally measured at 7, 14, and 28 days, and also at greater ages, especially when pozzolans are used. The rate of cement hydration reactions can be, and frequently is, changed intentionally by use of admixtures [12].

Corrosion inhibitors are admixtures which usually do more than just inhibit corrosion. They may influence initial set, later strength gain or other properties. The effects they produce in the field depend on conditions there—which may not be identical to conditions used in the laboratory. Changes in the time of addition of an admixture, or in the order of addition of two admixtures, can give different set times. For example, during laboratory tests with one commercial inhibitor based on calcium nitrite, a retarder and the corrosion inhibitor were added, simultaneously from two graduated cylinders, almost immediately after addition of water to cement. This technique was chosen to simulate the admixture addition expected in a ready-mix plant. A dosage level of retarder was determined which overcame the acceleration of the inhibitor and provided a little more retardation. When the test batches were scaled up to a concrete truck mixer, retarder was added similarly from a (large) graduated cylinder, right into the mixer during addition of water (the truck arrived "dry", containing only cement plus moist aggregate). Then a fork lift was brought into position to lift a pallet and several buckets of inhibitor to the top of the truck where the addition of inhibitor admixture was completed. The whole addition procedure took about 10 min. The combined admixture doses, which produced 1 or 2 h delays in set when added simultaneously in the lab, gave more than 18 h delay of set in the field when the admixtures were added separately. (Low overnight temperatures may have contributed to the delay.) Even after this extreme delay in set time, the truck-mixed concrete resumed normal hydration and before 28 days was stronger than the unretarded mixes, comparable to previous lab results. Later, concrete made in the laboratory according to the timing of the field test additions was found to reproduce the extended set times.

3.2. Air entrainment

Expansion due to freezing wet concrete may open cracks already begun by corrosion processes, and vice versa. Cracked concrete then allows ingress of water and chloride at a faster rate than uncracked concrete. Cracking due to freezing may be eliminated by use of air-entraining admixtures to provide small bubbles, closely spaced. Use of deicing salt implies freezing temperatures, so where salt is used on concrete, air will be deliberately entrained for protection. Corrosion inhibiting admixtures may have an effect on air content or its characteristics and a well-designed concrete mix will take this into account.

Some years ago, during the commercial introduction of a corrosion inhibitor, large-scale specimens for outdoor exposure at a remote test facility were made by an experienced contractor. Small specimens were cast at the same time and tested in the laboratory. Unexpectedly, the corrosion-inhibited specimens started failing the freeze–thaw test ASTM C-666 [13]. The test data showed that the strength of the inhibited mixes was considerably higher than the reference mixes, as expected. Air content had been specified to be the same for all batches in this series. But microscopic examination (linear traverse, ASTM C-457 [13]) showed that the inhibited mixes had air content *lower* than the reference concretes, insufficient to provide protection against freezing. According to the contractor, the *same* amount of air was added to all batches–but it was measured *as milliliters of air-entraining agent*. In this case, use of corrosion inhibitor required increasing the amount of air-entraining agent to provide the same volume per cent of entrained air in the concrete. The inhibited specimens had to be remade with a volume per cent of air comparable to the reference concrete—and then performed similarly well in the freeze–thaw test. On the other hand, some corrosion inhibitors will increase air content (reducing strength), and this might be corrected for by reducing the amount of air entrainer normally used, or by changing the mixing procedure or mix design, or by adding an air detrainer. In post-treatment (impregnation) applications, this is of no importance, because the hardened air structure has already been established in the concrete.

3.3. Permeability and diffusion

Low permeability, which results from a low water/cement ratio used in high strength concretes, reduces the ingress of chloride ion from external sources. When high strength concrete gives improved corrosion resistance, it is lower permeability, rather than mechanical strength, which is the source of the reduced corrosion threat. Permeability of concrete could be maintained at reasonably low values by specifying a minimum desired compressive strength [14]. Recent specifications [15] for high performance concrete to be used in bridges include charge passed (by AASHTO T-277, a measure of permeability), in addition to specifying strengths and 28-day drying shrinkage. Other diffusion tests have been proposed, but this is one of the easiest to perform [16]. Lower water/cement ratios may be obtained without loss of workability by use of water reducers or superplasticizers.

Lower permeability and increased strength can also be achieved by use of pozzolanic materials like silica fume, slag and fly ash (which are not in themselves corrosion inhibitors). The reduction in permeability can be a factor of 5 or 10 [2,17]. Pozzolans react with calcium hydroxide to produce more silicate binder; pozzolanic concretes therefore usually contain less cement than plain portland cement concrete of the same strength. Residual alkalinity, although less than in a comparable portland cement concrete, is generally adequate for passivation, and the reduced permeability is a distinct advantage. Addition of chemical water barriers or hydrophobic agents like calcium stearate emulsion, butyl stearate emulsion [18] or butyl oleate emulsion [19] to an admixture which has other corrosion preventatives can also reduce permeability of concrete. These esters are stable as an aqueous admixture, but in alkaline concrete will hydrolyze to an alcohol plus an insoluble, hydrophobic calcium salt (Eq. (5)). If the reaction occurs at the optimum time, the

$$\begin{aligned} &2\mathrm{C_4H_9\text{-fatty carboxylate}} + \mathrm{Ca(OH)_2} \\ &\quad = 2\mathrm{C_4H_9OH} + \mathrm{Ca(fatty\ carboxylate)_2} \end{aligned} \tag{5}$$

precipitate will line the pore walls, or block them entirely, with a layer of hydrophobic salt that resists further water penetration.

Fick's first law of diffusion (the amount of a material diffusing is proportional to the difference of concentration) applies to steady-state conditions. Fick's second law (Eq. (6), [20]) is more useful in actual corrosion situations (the increase in chloride concentration at the rebar divided by the time interval equals the diffusion coefficient times the concrete surface concentration of chloride divided by the concrete cover thickness squared:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = D \cdot \frac{\mathrm{d}^2 C}{\mathrm{d}x^2} \tag{6}$$

where: C = chloride concentration, D = diffusion coefficient, x = thickness of concrete cover, t = time.

The diffusion coefficient of chloride ion (typically in the range of 10^{-11}–10^{-13} m^2/s [2,4,17] increases by a factor of about 7 as the w/c ratio increases from 0.3 to 0.6. It also increases as temperature rises, with an activation energy ~35 kJ/mol, similar to chemical reactions in general. But it decreases with time, about a factor of two after ten years [2], as the cement continues to hydrate.

Permeability to ions is necessary for corrosion because the electrochemical character of corrosion has two parts: the electronic path (electrons pass through the steel from anode to cathode) and an ionic path (which allows the excess anionic species formed at the cathode (hydroxyl ions) to balance electric charges with the ferrous cations formed at the anode). The preexisting ions in the pore water of the concrete will do most of the charge-balancing, but if the porosity of the concrete is low, or if it is quite dry, corrosion current will be much reduced.

3.4. Chloride

The presence of chloride is implied when corrosion of reinforced concrete is discussed. One approach is to try to discover how to make its effects less harmful, to deactivate its catalytic action; another is to try to make the good effects of corrosion inhibitors better, to deactivate the rebar. There is significant overlap between these two approaches, and both approaches may even be used simultaneously.

Cement itself is thought to have the ability to bind some chloride ion, as Friedel's salt ($Ca_2Al(OH)_6Cl \cdot 2H_2O$, or $C_3A \cdot CaCl_2 \cdot 10H$), rendering it ineffective (or at least, less effective) as a catalyst for corrosion [3,4]. This leads to the concept of a threshold value for chloride [21],which is in the range of 1–1.6 pounds of chloride per cubic yard of concrete (0.6–1 kg/m^3) [22]. Below this level of chloride, the alkalinity of concrete is enough to minimize corrosion, although not eliminate it. A difficulty with relying on just the aluminates to bind chloride is that the threshold is small enough so that external chloride, if present to any significant extent, will eventually accumulate and exceed the threshold value. Predictive models based on theoretical considerations and actual results [23–25] estimate service lives for various alternatives, considering anticipated levels of chloride and structural features of the concrete.

3.5. Carbonation

The effect of carbon dioxide in reducing the pH of concrete (Eq. (7)) makes it

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \tag{7}$$

an accessory to corrosion—an active corrosive agent, rather than just a catalyst. In practice, however, carbonation of concrete causes problems (by reducing the pH and reducing the protection normally afforded by concrete) only when the cover over the steel is shallow and the concrete porous [4], neither of which reflect robust construction. In short, the corrosive effects of carbonation are relatively easily avoided. Corrosion occurring through the effects of chloride is a more serious concern in North America and the benefits from use of corrosion inhibitors are more visible.

4. Test procedures

4.1. Specimen size and aqueous environment

A simple way to investigate the corrosion process of steel is to substitute limewater for solid concrete [1]. Small rebar specimens can be tested in various solutions quickly and extensively with laboratory instrumentation. Making predictions about service life of field concrete based on time to corrode in limewater is not feasible, however, because the chemical environment about a rebar in limewater is significantly different from the environment in concrete. The composition and structure of field concrete changes with time as it continues to hydrate, as it picks up chloride ion, as it undergoes wetting and drying and endures mechanical stresses. Although these effects are not present in limewater tests, the results of these tests can be useful in determining levels of inhibitor and antagonist (chloride) to be used in larger-scale tests in mortar or concrete [1,26–28]. Larger scale tests with mortar or small-aggregate concrete commonly use 6 × 12 in. cylinders with imbedded rebar (frequently called "lollipops") and 11 × 6 × 4.5 in. prisms (ASTM G-109, [29]).

The three most common ways to bring chloride ion into contact with rebar in concrete are (1) to admix the chloride into the fresh concrete, (2) to immerse the hardened concrete in a salt solution, and (3) to pond the specimen (perhaps alternating with drying or surface-washing operations). Admixing the chloride allows immediate formation of Friedel's salt, tying up low concentrations of chloride or allowing higher concentrations immediate access to the rebar, whereas penetration by diffusion allows the rebar time to develop a more resistant passive film in an alkaline environment. Open-circuit potentials of rusted rebars generally require several hours to a day to settle down after being placed in fresh concrete, depending on the degree of surface rust and contamination.

Visible damage to concrete implies a late stage in the corrosion process. Measurement of open-circuit potential with a half-cell (ASTM C-876 [11]) is not just a laboratory test, but works in the field in the early stage of corrosion to map areas for observation and planning for later repair. A digital voltmeter with 10 MΩ input impedance is usually adequate. Electrical connection to the rebar mat is not necessary if two half-cell probes are used [26]. In the laboratory, different types of information may be obtained by determining macrocell current (ASTM G-109 [29,30], or polarization resistance. These two methods focus on the current which can be supplied by the anode; corrosion current correlates with the anode size and total extent of corrosion. Measurement of AC impedance goes one step further and measures capacitive effects in the current path; it has been used to shed light on diffusion processes [31–33]. Other instrumentation can be used for sweeping potential or current to determine film breakdown potentials and corrosion onset potentials on short time scales.

Potentials correlate well with corrosion current most of the time, but can be misleading under some conditions. For example, a small test series of concrete specimens was made with two rebars imbedded for macrocell current measurements (with and without inhibitor), and with excellent protection around the protruding rebar. The specimens were placed in a 100% humidity curing chamber. After a short time, the potentials of all specimens rose to very high negative values, apparently signifying very active corrosion, but without significant macrocell current. Examination of the rebars by splitting open the concrete showed no corrosion. The reason for the high negative potentials was finally attributed to complete saturation of the concrete with water, ultimately excluding oxygen. This raised the cathode resistance to such a high value that a very small anodic current was sufficient to develop a highly negative potential. The small current which does occur even in the absence of rust formation is probably related to maintenance of the passive film and eliminating defects [31]. The same effect (minimal corrosion) occurs in the deep ocean environment because of oxygen deprivation.

4.2. Stray currents

Stray potentials or applied electrical currents overcome protection that might be offered by an inhibitor and force corrosion to occur. Unless they are severely attenuated by low permeability or high resistance in the concrete, the enforced corrosion leads to rapid concrete failure. Accelerated corrosion studies run with applied current or high applied potentials (~10 V and more across the specimen) have correlated failures with permeability and tensile strength better than with any other property, but now see relatively little use [34]. Some useful information may be obtained from accelerated testing with challenge voltages in the millivolt range (up to a few hundred millivolts), but it is difficult to do this uniformly in large concrete specimens. (Polarization resistance measurements apply a voltage for a brief time to determine the degree of corrosion activity, in contrast to potentials or currents which are continuously applied to force corrosion.)

5. Corrosion inhibitors

5.1. Calcium nitrite

Calcium nitrite is the first corrosion inhibitor admixture commercialized on a large scale for reinforced concrete [21]. It first saw use in Japan, where it was used at relatively small doses to counter the salt present in sea sand used in construction of reinforced concrete. Sodium nitrite had been used for corrosion inhibition in non-concrete applications previously and was commercially available (and has been investigated in Europe), but the addition of such an alkali salt was not advantageous in concrete. The disadvantage of an alkali-metal salt admixture is even more pronounced now, as alkali levels in cements drift higher and as alkali-aggregate reactions become more prominent.

The first study of commercial calcium nitrite to be published [35] detailed its ability to increase 28-day strength by over 6% for each per cent of calcium nitrite added (by weight of cement), starting with a large increase at the 24 h test. Its acceleration of initial set was more than 2 h at 2% addition, and final set was accelerated by more than 3 h. These accelerations could be controlled by minor amounts of retarder to give set times as long as or longer than unadmixed concrete—with due attention paid to timing of admixture addition. Isothermal calorimeter curves of Type I and Type II cements were clearly shifted due to the accelerating effect of the calcium nitrite. Later studies showed that calcium nitrite is an effective corrosion inhibitor which always improves corrosion resistance, but which gives especially good performance at water-cement ratios below 0.5 [31].

The acceleration characteristic of calcium nitrite has proven so useful that a commercial accelerator admixture is available based on calcium nitrite. The purpose with this admixture is not primarily to *protect* steel from chloride, but simply to accelerate concrete without introducing the threat of chloride-induced corrosion. Another advantage is that 28-day strength is increased with calcium nitrite, not decreased as with calcium chloride.

Electrochemical measurements were unequivocal in showing that corrosion activity of steel was strongly reduced by low concentrations of nitrite, and that the amount of nitrite required to promote passivity rose in proportion to the concentration of chloride ion present [1]. The same study revealed the chemical reaction causing the corrosion inhibition (Eq. (8)):

$$Fe^{++} + 2OH^{-} + 2NO_2^{-} = 2NO + Fe_2O_3 + H_2O \qquad (8)$$

The reaction between ferrous sulfate solution and calcium nitrite solution occurs immediately. The product gas (NO) was recovered in 90% yield and identified by mass spectrometry, and by visual observation: the colorless gas can be observed to turn brown as it is poured out of a flask. In concrete, two more reactions are likely to occur, although no details have been published (Eqs. (9) and (10)):

$$2NO + O_2 = 2NO_2 \qquad (9)$$

$$2NO_2 + 2OH^{-} = NO_2^{-} + NO_3^{-} + H_2O \qquad (10)$$

Of equal interest are the reactions which do not proceed to any extent (Eqs. (11) and (12)):

$$Fe^{0} + NO_2^{-} = Fe^{0} + NO_2^{-} \qquad \text{(no reaction, [36])} \qquad (11)$$

$$Fe^{+++} + NO_2^{-} = Fe^{+++} + NO_2^{-} \qquad \text{(no reaction)} \qquad (12)$$

The stability of ferric ions in the presence of nitrite was proven by mixing solutions of ferric sulfate and calcium nitrite and filtering off the calcium sulfate precipitate. The resultant solution of ferric nitrite, kept in a clear glass bottle exposed to laboratory fluorescent light for over 15 years, only slowly developed a minimal black precipitate.

Calcium nitrite is identified as an anodic inhibitor because it functions at the anode, quickly oxidizing ferrous ions, the first product of corrosion, to ferric ions, which then precipitate in the alkaline pH of concrete. This rapid precipitation may better be described as a film repair unless some event causes a larger reaction. The precipitate and stifling action on a larger scale was seen in a 6 × 12 in. lollipop specimen of inhibited concrete which was studied by open circuit potential measurements. The rebar potential, initially in the passive range, slowly went moderately active after a few weeks (due to immersion in salt water), then became passive again and remained so for the duration of the test. At the conclusion of the test, this specimen had a passive potential, but it was split open and visually inspected because of its unusual behavior. The rebar was free of rust and in essentially the same condition as when it was imbedded—except for one small black spot adjacent to an air void in the concrete about 1 mm in diameter. The air void was tightly packed with black powder. The conclusion was that the air void (did it perhaps at one time fill with water?) somehow tipped the electrochemical balance so that an anode formed, driving the potential more negative. After a week or so, nitrite ion was able to diffuse to the site in sufficient quantity to oxidize and precipitate ferrous ions and reduce chloride mobility so that corrosion was stopped.

Prior to the US commercialization of calcium nitrite, Russian workers had studied a 50–50 mixture of calcium nitrite and calcium nitrate for use as a corrosion inhibitor [37].This blend is easier to produce than pure nitrite, for NO_2 gas (from oxidation of ammonia for production of nitric acid) may be bubbled into alkaline solution to give the blend of nitrite and nitrate (Eq. (10)). Preparation of pure calcium nitrite requires blending and introducing NO and NO_2 gases into a stirred suspension of $Ca(OH)_2$ so that they react in equimolar ratio (Eq. (13)). (Nitrogen tracer studies have shown rapid exchange between NO and NO_2 consistent with intermediate N_2O_3, but it is not isolated.) Typically, commercial production is balanced well enough to keep the calcium nitrate at 3% or less:

$$NO + NO_2 + 2OH^{-} = 2NO_2^{-} + H_2O \qquad (13)$$

Preliminary corrosion tests in limewater indicated the nitrite provided all the inhibition.

Below 55 °C, calcium nitrite, at concentrations above 20%, combines with calcium hydroxide to form a double salt (Eq. (14), [38]):

$$Ca(NO_2)_2 + Ca(OH)_2 + 2H_2O = Ca(NO_2)_2 \cdot Ca(OH)_2 \cdot 2H_2O \qquad (14)$$

Immersing concrete in admixture-grade calcium nitrite (30% concentration) can force double salt formation to occur, with consequent expansion and cracking of the concrete. Evidence of double salt formation does not appear in concrete when calcium nitrite is used at levels as high as 5% by weight of cement [33], or in impregnation experiments with ponded calcium nitrite [39], perhaps because the amount of calcium nitrite solution is only a few millimeters deep. In one study, observation of severe deterioration after 8 months, when water-saturated two-week old mortar specimens ($w/c = 0.63$) were soaked in saturated (>35%) calcium nitrite solution, was thought to be a problem [40], but when curing was extended to 2 months (in air), no deterioration was observed after eight months. It may be that cracking requires a weak mortar/concrete and a large excess of calcium nitrite solution at high concentration. Some concrete deterioration reported in a calcium nitrate fertilizer plant after 22 years exposure [41] may have been due to a similar double salt formation.

An analytical method has been published for the estimation of nitrite in concrete to assist regulatory agencies which require monitoring of admixed concrete for inhibitor addition [42]. Three techniques tested, ion chromatography, polarography and colorimetry, have comparable accuracy, but where resources permit, monitoring the addition during the batching operation eliminates the need for relatively tedious analyses.

5.2. Calcium nitrate

Recent work indicates that calcium nitrate may have some corrosion inhibiting properties of its own. Addition of calcium nitrate as a corrosion inhibitor in diesel fuel has been suggested [43]. Mortar prisms containing 3.85% calcium nitrate, exposed to wetting and drying three times with 5% NaCl solution, were shown by polarization resistance measurements to corrode five times slower than the reference mortar after 14 months of curing [44] Concrete cylinders 100 mm × 200 mm high, using additions of 2% and 4% calcium nitrate, with admixed chloride or cyclic wetting with 5% NaCl solution, were observed up to 51 months, and showed significant reduction in corrosion by visual inspection [41].

Nitrates do not have the extensive history of corrosion inhibition in concrete that nitrites have, except perhaps for the earlier Russian work [37]. Part of the reasoning behind looking into calcium nitrate is that the electrochemical relation between nitrite and nitrate is so energy-neutral (Eq. (15)):

$$2NO_3^- + 2H_2O + 4e^- = 2NO_2^- + 4OH^- \qquad E_0 = +0.01\ \mathrm{V} \tag{15}$$

There is some question, however, about the significance of this thermodynamic datum because, "unlike nitrite, nitrate does not appear to work when tested in a rapid solution test" [41]. It was pointed out that the electrochemical potential strongly favors nitrite oxidation to nitrate [44] (Eq. (16)),

$$2NO_2^- + O_2 = 2NO_3^- \qquad E_0 = +0.39\ \mathrm{V} \tag{16}$$

but later experiments [45] found no evidence of oxidation of nitrite at pH 13, and only a small trace of nitrate formation at pH 2; only at pH 1 was significant nitrate formed. This result agrees with concrete data which showed nitrite to be long lasting in concrete, being present at near original concentrations after 17 years [46].

A good reason for continuing the investigation of calcium nitrate as a corrosion inhibitor is its lower cost. Its widespread use as an accelerator [47] suggests at least that it is not harmful to concrete (except in very concentrated form [41]). The acceleration in set may be accompanied by a temporary compressive strength loss at 1 day, but the strength gain is quickly regained [44]. While the electrochemical data and visual examination are all encouraging, more work is needed to determine the mechanism behind the improvement in corrosion resistance. It may be that in spite of a superficial chemical resemblance to calcium nitrite, corrosion inhibition by calcium nitrate could occur by an entirely different process, perhaps one dependent more on the improved properties of the concrete. It should be noted that concrete grade calcium nitrate contains no ammonium nitrate, and is much preferred to the fertilizer grade, which contains more than 8% ammonium nitrate on a dry basis.

5.3. Cathodic inhibitors

5.3.1. Aminoalcohols

$H_2N{-}CH_2{-}CH_2{-}OH$	$(CH_3)_2N{-}CH_2{-}CH_2{-}OH$
Ethanolamine	Dimethylethanolamine

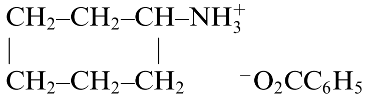
Aminoalcohols such as ethanolamine [48] and dimethylethanolamine control corrosion by attacking cathodic activity, blocking sites where oxygen picks up electrons and is reduced to hydroxyl ion. They may adsorb at anodic sites as well. One study [49] examined the inhibition effect of a commercially available complex inhibitor containing 15% nitrite and an aminoalcohol on Type 304 stainless steel electrodes immersed in limewater solutions for up to 72 h using a potentiostat. A synergistic effect was observed, combining the effect of nitrite on ferric ion precipitation with the known film-forming properties of hydroxyalkylamines. The corrosion current in the presence of 3% NaCl was reduced at pH 12.67 by a factor of 2.5 and at pH 9.37 by a factor of 5.4. A larger scale investigation might show whether this ratio could be improved with black steel rebar, since the stainless steel may have been fairly resistant to corrosion even without inhibitor. Exceptionally good corrosion resistance in the reference system would leave less room for improvement by the inhibitor.

N,*N*-dimethylethanolamine (DMEA) is used to protect rebar in concrete in commercial corrosion inhibitors [50]. X-ray photoelectron spectroscopy was used to examine steel surfaces which were first cut, polished and oxidized and then immersed in solutions of sodium chloride and DMEA. Electrons ejected from the 1s levels of carbon, nitrogen and oxygen, and from the 2p levels of iron and chlorine, were analyzed to estimate surface concentrations of these species. Below 1 M (about 9% by weight), DMEA adsorbed on the steel oxide surface in slightly more than monolayer thickness (between 0.75 and 0.9 nm). Higher concentrations (>2 M) cause more adsorption, but only up to a bilayer thickness. DMEA is strongly and irreversibly adsorbed and cannot be completely rinsed off the iron oxide surface. Immersion of steel in solutions containing both DMEA and NaCl for 5 min was sufficient to reach equilibrium; DMEA was found to partially displace chloride from the iron oxide surface. These observations suggest that inhibition of corrosion occurs through a mechanism whereby DMEA displaces chloride ion and forms a durable passivating film. In this view, although the aminoalcohols adsorb on non-corroding sites which may seem more cathodic than anodic, they can just as easily be said to adsorb on potentially anodic sites.

An organic corrosion inhibitor (OCI) comprising an aqueous emulsion of esters and aminoalcohol (according to the Material Safety Data Sheet), is a mixed inhibitor, affecting corrosion through a combination of active and passive mechanisms. A study extending over a decade investigated the active part, a film-forming aminoalcohol [51] which is generally taken to be a cathodic inhibitor. The passive part of the OCI mechanism reduces permeability by hydrolysis of an organic ester and deposition of insoluble calcium salts of fatty acid which hydrophobe the concrete pores to reduce ingress of chloride ions (Eq. (5)). A reduction of 56% in the capillary absorption rate was seen for the OCI-treated concrete. The OCI admixture reduces the chloride build-up rate, reduces the chloride diffusion coefficient, moderately increases the chloride threshold and slows the rate of corrosion after initiation. The insoluble salts appear to have long persistence in the concrete.

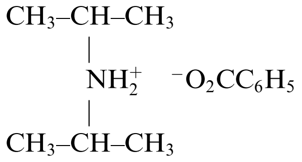
5.4. Other cathodic agents

Migrating corrosion inhibitors, based on amine carboxylate chemistry, may be incorporated as an admixture during new construction or applied as a surface impregnant on existing structures [52]. It is thought that these inhibitors migrate through concrete pores to the rebar surface where a monomolecular layer is adsorbed. Half-cell and macrocell measurements seem to confirm corrosion protection. It was concluded that migrating corrosion inhibitors are compatible with concrete and with additives used in concrete and can play an important role in delaying corrosion of reinforcement steel. The chemistry of this admixture is protected by trade secret, but certain generic corrosion inhibitors may be related, e.g., cyclohexylammonium benzoate and diisopropylammonium benzoate. In both cases, the amine is liberated under alkaline conditions and may migrate to sites on a rebar. Benzoate ion is itself a corrosion inhibitor, especially at high pH, probably by adsorbing on active sites.



$$\begin{array}{l} CH_2\text{–}CH_2\text{–}CH\text{–}NH_3^+ \\ |\qquad\qquad\qquad | \\ CH_2\text{–}CH_2\text{–}CH_2 \qquad {}^-O_2CC_6H_5 \end{array}$$

Cyclohexylammonium benzoate



$$\begin{array}{l} CH_3\text{–}CH\text{–}CH_3 \\ \qquad\quad | \\ \qquad\quad NH_2^+ \quad {}^-O_2CC_6H_5 \\ \qquad\quad | \\ CH_3\text{–}CH\text{–}CH_3 \end{array}$$

Diisopropylammonium benzoate

References

[1] Rosenberg AM, Gaidis JM. The mechanism of nitrite inhibition of chloride attack on reinforcing steel in alkaline aqueous environments. Mater Performance 1979;18(11):45–8.

[2] Pourbaix M. Atlas of electrochemical equilibria in aqueous solutions. Oxford: Pergamon Press; 1966. p. 553.

[3] BirninYauri UA, Glasser FP. Friedel's salt: its solid solutions and their role in chloride binding. Cem Concr Res 1998;28(12):1713–23.

[4] Rosenberg A, Hansson CM, Andrade C. Mechanisms of corrosion of steel in concrete. In: Skalny JP, editor. Materials science of concrete I. The American Ceramic Society; 1989. p. 285–313.

[5] Gartner EM, Gaidis JM. Hydration mechanisms I. In: Skalny JP, editor. Materials science of concrete I. The American Ceramic Society; 1989. p. 95–126.

[6] Lorrain M. Bond performance of high performance concrete. In: Malier Y, editor. High performance concrete. London: E&FN Spon; 1994.

[7] Pyc WA, Weyers RE, Sprinkel MM, Weyers RM, Mokarem DW, Dillard JG. Performance of epoxy-coated reinforcing steel. Concr Int 2000;22(2):57–62.

[8] Manning DG. Corrosion performance of epoxy-coated reinforcing steel: North American experience. Construct Building Mater 1996;10(5):349–65.

[9] McHattie JS, Perez IL, Kehr JA. Factors affecting cathodic disbondment of epoxy coatings for steel reinforcing bars. Cem Concr Compos 1996;18:93–103.

[10] Edwards DL. HPC on bridges: the Florida experience. Concr Int 2000;22:63–5.

[11] Trauenberg SE, Foley RT. J Electrochem Soc 1971;118:1066.

[12] Lankard DR. Cement and concrete technology for the corrosion engineer. Mater Performance 1976;15(8):24–37.

[13] Annual Book of ASTM Standards, vol. 04.02. Philadelphia: American Society for Testing and Materials, 1989.

[14] Rosenberg AM, Gaidis JM. Corrosion inhibiting concrete composition. US Patent No. 4,285,733, 25 August 1981.

[15] Finnerty P, Stewart V, Meyers R. HPC Bridge Views, vol. 18. Nov/Dec 2001. p. 1.

[16] Streicher PE, Alexander MG. A critical evaluation of chloride diffusion test methods for concrete. In: Third CANMET/ACI International Conference on Durability of Concrete, Ottawa 1994. p. 517–30.

[17] Thomas MDA, Bamforth PB. Modelling chloride diffusion in concrete. Effect of fly ash and slag. Cem Concr Res 1999;29:487–95.

[18] Mailvaganem NP. Admixtures. In: Mailvaganem NP, editor. Repair and protection of concrete structures. Boca Raton: CRC Press; 1991 [chapter 6].

[19] Berke NS, Weil TG. World wide review of corrosion inhibitors in concrete. In: Malhotra VM, editor. Advances in concrete technology. Ottawa: CANMET; 1994.

[20] Amey SL, Johnson DA, Miltenberger MA, Farzam H. Predicting the service life of concrete marine structures: an environmental methodology. ACI Struct J 1998;95(2):205–14.

[21] Nmai CK, Farrington SA, Bobrowski GS. Organic-based corrosion-inhibiting admixture for reinforced concrete. Concr Int 1992;14(4):45–51.

[22] Berke NS, Pfeifer DW, Weil TG. Protection against chloride-induced corrosion. Concr Int 1988;10(12):45–55.

[23] LIFE 365 v1.1. A model available from the Concrete Corrosion Inhibitors Association at the website www.corrosioninhibitors.org.

[24] Sagues AA, Kranc SC, Washington BG. Computer modelling of corrosion protection of steel in concrete. In: Dhir RK, Jones MR, editors. Concrete 2000, vol. 2. London: E&FN Spon; 1993. p. 1275–84.

[25] Tuutti K. ArmeringsKorrosion—Betongkonstruktioners livslangd. Nordisk Betong 1980;5–6:6–10.

[26] Gaidis JM, Rosenberg AM, Saleh I. Improved test methods for determining corrosion inhibition by calcium nitrite in concrete. In: Corrosion of reinforcing steel in concrete.Tononi DE, Gaidis JM, editors. ASTM STP 713. American Society for Testing and Materials; 1980. p. 64–74.

[27] Gaidis JM, Rosenberg AM. The inhibition of chloride-induced corrosion in reinforced concrete by calcium nitrite. Cem Concr Aggreg 1987;9(1):30–3.

[28] Rosenberg AM, Gaidis JM. Methods of determining corrosion susceptibility of steel in concrete. Transp Res Record 1978;692:28–34.

[29] Annual Book of ASTM Standards, vol. 03.02. Philadelphia: American Society for Testing and Materials, 1996.

[30] Berke NS, Shen DF, Sundberg KM. Comparison of the polarization resistance technique to the macrocell corrosion technique. In: Corrosion rates of steel in concrete.Berke NS, Chaker V, Whiting D, editors. ASTM STP 1065. Philadelphia: American Society for Testing and Materials; 1990. p. 38–51.

[31] Berke NS. The effects of calcium nitrite and mix design on the corrosion resistance of steel in concrete. Part I: Paper #273 in Corrosion '85, Boston, 1985; Part II: Paper #132 in Corrosion '87, San Francisco, 1987.

[32] Bentur A, Diamond S, Berke NS. Steel corrosion in concrete. London: E&FN Spon; 1997. p. 76–87.

[33] Berke NS. Corrosion rates of steel in concrete. ASTM Standardization News, 1986. p. 57–61.

[34] Rosenberg AM, Gaidis JM. Methods of determining corrosion susceptibility of steel in concrete. Transp Res Record 1979;692: 28–34.

[35] Rosenberg AM, Gaidis JM, Kossivas TG, Previte RW. A corrosion inhibitor formulated with calcium nitrite for use in concrete. In: Chloride corrosion of steel in concrete. Tonini DE, Dean Jr SW, editors. ASTM STP 629. American Society for Testing and Materials; 1977. p. 89–99.

[36] Cohen M, Pyke RJ. J Electrochem Soc 1948;93:63.

[37] Ratinov VB, Enisherlova SG, Zagirova RU. Prom Stroit 1970;(7):13–5 [Chem. Abs. 73:101728f];
Solomentseva NS, Enisherlova SG. Tr Mosk Avto Dorozh Inst 1972;(46):66–72 [Chem. Abs. 80:124125r];
Tokar VB, Rozenberg TI, Ratinov VB. Inhibitory Korroz Met 1972:199–203 [Chem. Abs. 83:32315m];
Ratinov VB, Novgorodskii VI, Ostrovskii AB. Beton i Zhelezobeton 1973;(12):18–20 [Chem. Abs. 80:99559a];
Enisherlova SG et al. Probl Antikorroz Zashch 1973:129–34 [Chem. Abs. 82:144266g];
Meilakh AG et al. SbTr-Nauchno-Issled Inst Prom Stroit (Ufa) 1974;15:57–60 [Chem. Abs. 84:184164v];
Akimova KM, Ivanov FM. Beton I Zhelezobeton (Moscow) 1976;(2):38–9 [Chem. Abs. 85:148159j].

[38] Gaidis JM, Rosenberg AM. Process for forming calcium nitrite. US Patent No. 4,294,813, 13 October 1981 [and references therein].

[39] Berke NS, Dallaire MP, Weyers RE, Henry M, Peterson JE, Powell B. Impregnation of concrete with corrosion inhibitor. In: Corrosion forms and control for infrastructure. Chaker V, editor. ASTM STP 1137. Philadelphia: American Society for Testing and Materials; 1992.

[40] Hope BB, Thompson SV. Damage to concrete induced by calcium nitrite. Mater J 1995;92(5).

[41] Justnes H. Calcium nitrate as corrosion inhibitor for reinforced concrete. In: Proceedings of the Ninth Middle East Corrosion Conference and Exhibition, NACE, 12–14 February 2001, Bahrain. p. 687–95.

[42] Jeknavorian AA, Chin D, Saidha L. Determination of a nitrite-based corrosion inhibitor in plastic and hardened concrete. Cem Concr Aggreg 1995;17(1):48–54.

[43] Rahway NJ. The Merck index. Merck & Co. Inc.; 1989.

[44] Justnes H, Nygaard EC. The influence of technical calcium nitrite additions on the chloride binding capacity of cement and the rate of chloride induced corrosion of steel embedded in mortars. In: Proceedings of the International Conference on Corrosion and Corrosion Protection of Steel in Concrete, vol. I, Sheffield, UK, 25–28 July 1994. p. 491–502.

[45] Justnes H, Nygaard EC, Grostad T. Calcium nitrite as a retarder of chloride initiated rebar corrosion. In: Swamy RN, editor. Proceedings of the International Conference "Infrastructure Regeneration and Rehabilitation. Improving the Quality of Life Through Better Construction. A Vision for the Next Millenium", Sheffield, UK, 28 June–2 July 1999. p. 189–98.

[46] Powers RG, Sagues AA, Cerlanek WD, Kasperand CA, Li L. Time to corrosion of reinforcing steel in concrete containing calcium nitrite. Final Report FHWA-RD-99-145, October 1999. 46p.

[47] Tokar V. Additive composition for Portland cement materials. US Patent No. 4,337,094, 29 June 1982.

[48] Martin P, Miksic BA. Corrosion inhibition in reinforced cement. Canadian Patent No. 1,258,473, August 1989.

[49] Munteanu VF, Kinney FD. Corrosion inhibition properties of a complex inhibitor—mechanism of inhibition. CANMET 2000, Ottawa. p. 255–69.

[50] Welle A, Liao JD, Kaiser K, Grunze M, Maeder U, Blank N. Interactions of *N*,*N*′-dimethylaminoethanol with Steel surfaces in alkaline and chlorine containing solutions. Appl Surf Sci 1997;119:185–90 [referring to Sika Armatec ®].

[51] Buffenbarger JK, Miltenberger MA, Miller BD, Casal HL. Long-term performance of an organic corrosion inhibitor. In: International Congress on Advanced Materials their Processes and Applications, Munich, Germany, 2000.

[52] Bjegovic D, Miksic B (CORTEC). Migrating corrosion inhibitor protection of concrete. Mater Performance 1999;38(11):52–56.